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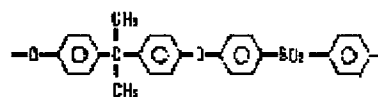
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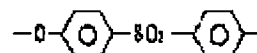
## (54) PRODUCTION OF POLYSULFONE RESIN SEMIPERMEABLE MEMBRANE

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a membrane whose water-permeability and fractional molecular weight can be made to be a wide range and in which choking and staining hardly occur by using a solution in which a polysulfone resin and a hydrophilic polymer are mixed and dissolved as a film forming dope and thermally cross-linking the formed film.



**SOLUTION:** As for a polysulfone resin having formula I and II as a composition component of a film forming dope, any range of the concentration is acceptable if it is sufficient to form a film and given proper characteristics to the film. However, due to the necessity to cover the decrease the polymer concentration to obtain high water-permeability and high fractional molecular weight, it is preferably that the concentration of the polysulfone resin is about 5-20%. It is proper that the addition amount of polyvinylpyrrolidone as a hydrophilic polymer is 3-10wt.%, through it also depends on the molecular weight.



In the case that these two polymers are mixed and dissolved in a solvent and then water is added as an additive, the addition amount of water should be about 1-5wt.% since coagulation property of the polysulfone resin is high. The addition amount of the hydrophilic polymer may be lessened by adding the fourth component.

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**CLAIMS**

[Claim(s)]

[Claim 1] The manufacture approach of the polysulfone system resin semipermeable membrane characterized by carrying out heat bridge formation of the film which fabricated polysulfone system resin and a hydrophilic macromolecule, using the solution which carried out the mixing dissolution as a film production undiluted solution.

[Claim 2] The manufacture approach of polysulfone system resin semipermeable membrane according to claim 1 that a hydrophilic giant molecule is a polyvinyl pyrrolidone.

[Claim 3] the solution which carried out the mixing dissolution of polysulfone system resin and the hydrophilic macromolecule -- this polysulfone system resin -- receiving -- a non-solvent -- or -- a swelling agent -- the manufacture approach of the polysulfone system resin semipermeable membrane according to claim 1 or 2 characterized by using the system which added the additive as a film production undiluted solution.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which this invention belongs] This invention relates to the manufacture approach of polysulfone system resin semipermeable membrane.

[0002]

[Description of the Prior Art] Conventionally, as a material of semipermeable membrane, many high molecular compounds, such as a cellulose acetate polyacrylonitrile polymethylmethacrylate polyamide, have been used. On the other hand, although originally used as engineering plastics, since polysulfone system resin has the heat-resistant stability, acid-proof and alkali resistance and biocompatibility, and good resistance to contamination, it attracts attention as a semipermeable membrane material.

[0003] JP,58-104940,A etc. is conventionally proposed as an approach of obtaining the semipermeable membrane using polysulfone system resin in for example, journal OBU applied polymer Science (20 volumes, 2377-2394 pages, 1976) and (said 21 volumes, 1883-1900 pages and 1977). However, since this resin has too strong intermolecular cohesive force and blockades a surface hole and the internal hole which should be penetrated, control of hole formation becomes difficult. For this reason, only the thing with a as small and cut off molecular weight which also has small water permeability as [ or less ] 100,000 is obtained. On the other hand, the following means are proposed in recent years as an attempt which opens a big hole in a front face by the film using polysulfone system resin.

[0004] \*\* How to use the microfacies separation between different-species polymers. (JP,48-176,B, JP,54-144456,A, a 57-50506 official report, a 57-50507 official report, 57-50508 official report)

\*\* How to have an extract and elution actuation after film production. (JP,54-26283,A, a 57-35906 official report, 58-91822 official report)

\*\* How to produce a film in the state of metastable liquid distribution of a film production undiluted solution. (JP,56-154051,A, a 59-58041 official report, a 59-183761 official report, 59-189903 official report)

\*\* How to put creativity at the time of spinning (JP,59-228016,A)

However, by the approach of \*\*, it has come to obtain a 100,000 or more-cut off molecular weight big hole only by using the difference in the coagulation rate between polymers. In order to blend in large quantities moreover, the original good engine performance of polysulfone system resin is easy to be lost. Moreover, the approach of \*\* is eluted, it is large and an extract and the inorganic granulation of blend polymer are classified into two approaches. In the former, although the polyethylene glycol and the polyvinyl pyrrolidone were main polymers, obtaining sufficient aperture and extract operation were difficult. In the latter example, silica powder is mixed, elution is carried out after film production by said JP,58-91822,A, using alkali, and it is 0.05 micrometers. Although it has succeeded in opening the above big hole, by this manufacture approach, the film which takes other pore size distribution from the same film production undiluted solution cannot be manufactured. \*\* Just before an approach mixes the non-solvent or swelling agent of polysulfone system resin in large quantities to a film production undiluted

solution and this film production undiluted solution carries out phase separation, it is a thing which it is and which produces a film by the way. By this approach, there is a fault which cannot use the temperature effect of a coagulation bath advantageously. \*\* Although an approach is spraying the wind of high humidity at the time of film production and aperture expansion in this front face is realized, if there is the effectiveness only in one side and it results especially in a hollow fiber, by this approach, only the thing of the range where a cut off molecular weight is small is obtained.

[0005] The manufacture approach of the polysulfone system resin semipermeable membrane of these former has the description in which the film production undiluted solution carries out phase separation at low temperature. For this reason, even if it gathered the rate of exchange of the non-solvent in a coagulation bath, etc. and the good solvent in the film and raised coagulation bath temperature utterly at the time of film production, in order that a film production undiluted solution might carry out balanced migration to the direction of a homogeneous system, it was what has the fault that a compact layer tends to be made on a front face, and the fault that the various semipermeable membrane which has broadly water permeability and a cut off molecular weight from the same undiluted solution cannot be manufactured.

[0006]

[Problem(s) to be Solved by the Invention] this invention persons analyzed the above-mentioned fault, and as a result of inquiring wholeheartedly, they reached this invention. It aims at offering the manufacture approach of the polysulfone system resin semipermeable membrane which can take water permeability and a cut off molecular weight broadly, and neither loading nor dirt can start especially easily.

[0007]

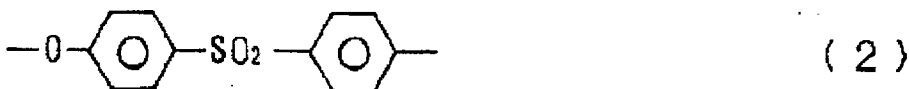
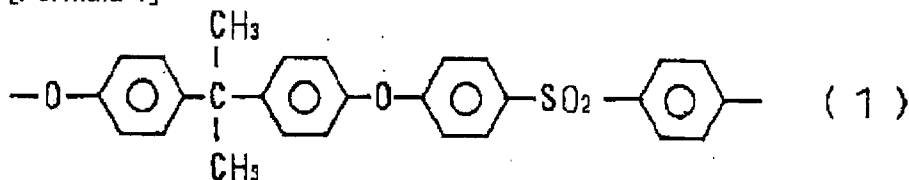
[Means for Solving the Problem] This invention has the next configuration. Namely, the "manufacture approach of the polysulfone system resin semipermeable membrane characterized by carrying out heat bridge formation of the film which fabricated polysulfone system resin and a hydrophilic macromolecule, using the solution which carried out the mixing dissolution as a film production undiluted solution."

[0008]

[Embodiment of the Invention] The film production undiluted solution used in order to manufacture polysulfone system resin semipermeable membrane in this invention consists of 3 component systems which consist of polysulfone system resin, a hydrophilic macromolecule, and a solvent fundamentally. Furthermore, it is also desirable to add an additive into a membrane formation undiluted solution.

[0009] the polysulfone system resin said here -- usually -- a formula (1) -- or (2) --

[Formula 1]



Although it consists of a \*\*\*\*\* unit, the functional group is included, or you may be the thing of an alkyl system and it does not limit especially.

[0010] A hydrophilic macromolecule is a macromolecule which there are polysulfone system resin and compatibility and has a hydrophilic property. Although a polyvinyl pyrrolidone is the best and a denaturation polyvinyl pyrrolidone, a copolymerization polyvinyl pyrrolidone, polyvinyl acetate, a polyethylene glycol, etc. are mentioned to others, it is not limited to these.

[0011] Both solvents are solvents which dissolve polysulfone system resin and a hydrophilic macromolecule. Dimethyl sulfoxide, dimethylacetamide, dimethylformamide, an N-methyl-2-

pyrrolidone, the dioxane of dimethylacetamide, dimethyl sulfoxide, dimethylformamide, and an N-methyl-2-pyrrolidone, etc. are especially desirable although various solvents are used.

[0012] If an additive has a solvent and compatibility, and serves as a good solvent of a hydrophilic macromolecule and it becomes the non-solvent of polysulfone system resin, or a swelling agent, anything, it is good, for example, has water, methanol, ethanol, isopropanol, hexanol, 1, and 4-butanediol etc. Considering a production cost, water is the most desirable. What is necessary is just to choose an additive, after taking the freezing characteristic over polysulfone system resin into consideration.

[0013] Easy for men of the same trade considers the combination which is arbitrary in each as for these combination, and has the above-mentioned property. Moreover, the mixed stock of two or more kinds of compounds is sufficient as a solvent and an additive.

[0014] As a presentation of this film production undiluted solution, polysulfone system resin is 5 - 50 % of the weight that what is necessary is just the density range which can produce a film and has a property as film. In order to obtain high water permeability and a big cut off molecular weight, polymer concentration should be lowered and is 5 - 20 % of the weight desirably in this case. It becomes impossible to obtain sufficient viscosity of a film production undiluted solution, but to form the film at less than 5 % of the weight. Moreover, if 50 % of the weight is exceeded, it will be hard coming to form a through tube.

[0015] In the case of a polyvinyl pyrrolidone, the thing of molecular weight 360,000, 160,000, 40,000, and 10,000 is marketed from GAF, as for especially the hydrophilic giant molecule, it is convenient to use this, but the thing of the other natural molecular weight may be used for it. However, as one of the reasons of addition of a hydrophilic macromolecule, for a certain reason, the thickening effectiveness is also so little that an addition uses the thing of the amount of macromolecules, good, and since the inversion of the temperature dependence of a phase separation phenomenon also becomes remarkable again, in order to obtain the permeable high film, it is advantageous. One to 20% of the weight, although especially the addition of a polyvinyl pyrrolidone has 3 - 10 desirable % of the weight, it is influenced by the molecular weight of the polyvinyl pyrrolidone to be used. When there are generally too few additions, and molecular weight is too low, if the inversion phenomenon of phase separation is difficult to get, polymer concentration is high and polymer molecular weight is too large, washing after film production will become difficult. So, it also becomes one approach to mix that from which molecular weight differs, to carry out a role assignment, and to use.

[0016] The mixed dissolution of the two macromolecules is carried out above at a solvent. Since it is high, 1 - 5 % of the weight has freezing characteristic desirable especially especially in the case of water although it is desirable to add an additive here 7 or less % of the weight for polysulfone system resin. When using an additive with small freezing characteristic, it is guessed easily that an addition increases.

[0017] In this invention, since this 4th component is added, the amount of a hydrophilic macromolecule can be lessened. The phase separation temperature of a film production undiluted solution falls as the concentration of an additive becomes high. What is necessary is just to set up low phase separation temperature, in order to obtain high water permeability and cut off molecular weight and to promote phase separation powerfully at the time of film production that what is necessary is just to make a setup of phase separation temperature into \*\*\*\* by the water permeability of the film for which it asks, or the cut off molecular weight. Moreover, the same effectiveness is acquired even if it makes temperature of a coagulation bath high. Since the film production undiluted solution used by this invention serves as a homogeneous system at low temperature, its undiluted solution stability is also good.

[0018] Polysulfone system resin semipermeable membrane is obtained under the above conditions. Film production actuation should just use a well-known technique. About a flat film, this film production undiluted solution is flowed on a flat substrate, and it is immersed into a coagulation bath after that. About a hollow fiber, in order to maintain a hollow gestalt, infusion is used, although it is [ spinning stability ] better to use a thing lower than the high thing of freezing characteristic for infusion to a film production undiluted solution -- coagulation bath

temperature and phase separation temperature, and a mouthpiece — what is necessary is just to decide the best presentation suitably, since the smooth nature of a hollow fiber wall changes by correlation with temperature. Hydrocarbons, such as the inactive Deccan octane undecane, may be used for polysulfone system resin. Moreover, a gas may be poured in and a hollow gestalt may be made to hold. Dry type length is 0.1–20cm, and 0.5–5cm is [ spinning stability ] still more desirable especially well. When a film is produced on the same presentation and the same conditions, the diameter of the hole which the flat film punctures on a front face from a hollow fiber tends to become large.

[0019] When the polysulfone system resin semipermeable membrane obtained by this approach makes a hydrophilic macromolecule remain in the film, it comes to give insolubilization processing to water by improving water wettability and constructing a bridge by heat.

[0020]

[Example] still more detailed [ in this invention ] by the following examples — it explains.

[0021] Hereafter, the used measuring method is as follows.

[0022] (1) In the case of the permeable hollow fiber, this hollow fiber was inserted in the glass case which equipped both ends with the hole for ring current liquid, it produced the small module using the commercial potting agent, and measured permeable ability by the approach of compute from the amount of the water of fixed time amount which keeps at 37 degrees C, pours water pressure on the hollow filament inside, and is penetrated outside through the film, an effective film surface product, and the differential pressure between film.

[0023] In the case of the flat film, it measured similarly using the churning cylinder cel.

[0024] The example 1 polysulfone (YUDERU P-3500) 15 section, polyvinyl-pyrrolidone (K90) 8 section, 1, and 4-butanediol 7 section was added to the dimethylacetamide 70 section, and the heating dissolution was carried out. Minute amount addition was carried out further and this film production undiluted solution prepared 1 and 4-butanediol so that phase separation might be carried out at 70 degrees C. the mouthpiece which consists the prepared undiluted solution of an annular orifice with an outer diameter [ of 1.0mm ], and a bore of 0.7mm — it breathes out, pouring in dimethylacetamide / water =85/15 as infusion from the inside of a hole — making — a mouthpiece — the coagulation bath which has water which kept it warm at 51 degrees C caudad installed 1.0cm from the field was passed, it rolled round to the skein after rinsing by the usual approach, and the hollow line-of-thread film was obtained. The mouthpiece kept it warm at 60 degrees C. The water permeability of the obtained hollow fiber showed the engine performance of 1320 ml/m<sup>2</sup> and hr-mmHg.

[0025] Furthermore, when 175 degrees C of this hollow fiber were processed for 5 hours and heat bridge formation of the polyvinyl pyrrolidone was carried out, water permeability became 15800ml / m<sup>2</sup>, and hr-mmHg. When the eluting material test after rinsing was performed, there was almost no effluent.

[0026] The example of comparison 1 polysulfone 12 section and the polyvinyl-pyrrolidone 6 section were added to the N-methyl pyrrolidone 82 section, and the heating dissolution was carried out. This undiluted solution was kept warm at 50 degrees C, and the film was produced like the example 1. Water permeability was as low as 600 ml/m<sup>2</sup> and hr-mmHg.

[0027] With the undiluted solution of the example 1 of example of comparison 2 comparison, it maintained at the undiluted solution and the room temperature, and the film was produced similarly. Water permeability was 250 ml/m<sup>2</sup> and hr-mmHg.

[0028] Although the water 2 section was added to the example of comparison 3 polysulfone 15 section, and the dimethylacetamide 83 section, the heating dissolution was carried out and the film was produced like the example 1 of a comparison, only what has as low water permeability as 25 ml/m<sup>2</sup> and hr-mmHg was obtained.

[0029] When it gave the film of the examples 1–2 of example of comparison 4 comparison with the extract of a polyvinyl pyrrolidone, and heat bridge formation processing, most water permeability was set to 0.

[0030]

[Effect of the Invention] This invention can take broadly the water permeability of polysulfone

system resin semipermeable membrane, and a cut off molecular weight. The base material of bipolar membrane can also be manufactured by choosing undiluted solution conditions and film production conditions appropriately. And to loading and dirt, since it is strong, the polysulfone system resin semipermeable membrane obtained can be used as a general industrial use way and a constituent-of-blood demarcation membrane of a medical field from a reverse osmotic membrane to high performance ultrafiltration membrane (or micro filter).

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(54)【発明の名称】 ポリスルホン系樹脂半透膜の製造方法

(57)【要約】

【課題】高透水性を有し、かつ親水性高分子が水不溶化されたポリスルホン系樹脂半透膜の製造方法を提供する。

【解決手段】ポリスルホン系樹脂と親水性高分子を混和溶解した溶液を製膜原液として用い、成形した膜を熱架橋することを特徴とするポリスルホン系樹脂半透膜の製造方法。

【特許請求の範囲】

【請求項1】ポリスルホン系樹脂と親水性高分子を混和溶解した溶液を製膜原液として用い、成形した膜を熱架橋することを特徴とするポリスルホン系樹脂半透膜の製造方法。

【請求項2】親水性高分子が、ポリビニルピロリドンである請求項1記載のポリスルホン系樹脂半透膜の製造方法。

【請求項3】ポリスルホン系樹脂と親水性高分子を混和溶解した溶液に該ポリスルホン系樹脂に対して非溶媒もしくは膨潤剤なる添加剤を加えた系を製膜原液として用いることを特徴とする請求項1または2記載のポリスルホン系樹脂半透膜の製造方法。

【発明の詳細な説明】

【0001】

【本発明の属する技術分野】本発明は、ポリスルホン系樹脂半透膜の製造方法に関する。

【0002】

【従来の技術】従来、半透膜の素材としては、セルロースアセテート・ポリアクリロニトリル・ポリメタクリル酸メチル・ポリアミド等多数の高分子化合物が用いられてきた。一方、ポリスルホン系樹脂は、元来エンジニアリングプラスチックとして使用されてきたが、その耐熱安定性、耐酸・耐アルカリ性、そして生体適合性、耐汚染性が良好であることから、半透膜素材として注目されている。

【0003】ポリスルホン系樹脂を用いた半透膜を得る方法として従来より例えば、ジャーナル・オブ・アプライド・ポリマー・サイエンス（20巻、2377～2394頁、1976年）及び、（同21巻、1883～1900頁、1977年）、特開昭58-104940号公報等が提案されている。しかし該樹脂は、分子間凝集力が強すぎて、表面の孔や貫通すべき内部の孔を閉塞してしまうため孔形成の制御が困難となる。このため、分画分子量が10万以下と小さくかつ透水性も小さいものしか得られていない。一方、近年、ポリスルホン系樹脂を用いた膜で、表面に大きな孔をあける試みとして、次のような手段が提案されている。

【0004】① 異種ポリマー間のマイクロ相分離を利用する方法。（特公昭48-176号公報、特開昭54-144456号公報、同57-50506号公報、同57-50507号公報、同57-50508号公報）

② 製膜後、抽出・溶出操作を有する方法。（特開昭54-26283号公報、同57-35906号公報、同58-91822号公報）

③ 製膜原液の準安定液体分散状態で製膜する方法。（特開昭56-154051号公報、同59-58041号公報、同59-183761号公報、同59-189903号公報）

16号公報）

しかし、①の方法ではポリマー間の凝固速度の違いを利用しているのみで、分画分子量10万以上の大きな孔を得るに至っていない。その上、大量にブレンドするため、ポリスルホン系樹脂の本来の良好な性能が失われやすい。また、②の方法は、ブレンドポリマーの抽出と無機顆粒を溶出する大きく2つの方法に分類される。前者においては、ポリエチレングリコール、ポリビニルピロリドンが主たるポリマーであるが、十分な孔径を得ることや抽出操作が困難であった。後者の例では、前記特開昭58-91822号公報で、シリカパウダーを混入して製膜後、アルカリを用いて溶出させ、0.05 $\mu$ m以上の大きな孔をあけるのに成功しているが、この製造方法では同一製膜原液から他の孔径分布をとる膜を製造することはできない。③の方法は製膜原液にポリスルホン系樹脂の非溶媒もしくは膨潤剤を大量に混合し、該製膜原液が相分離する直前のところで製膜するものである。かかる方法では、凝固浴の温度効果を有利に利用できない欠点がある。④の方法は、製膜時に高湿度の風を吹きつけることで、該表面での孔径拡大を実現しているが、該方法では片面にしかその効果はなく、特に中空糸膜に至っては、分画分子量は小さい範囲のものしか得られない。

【0005】これら従来のポリスルホン系樹脂半透膜の製造方法は、その製膜原液が低温で相分離する特徴を有するものである。このため製膜時に凝固浴中の非溶媒等と膜中の良溶媒との交換速度を上げようとして凝固浴温度を上げても製膜原液が均一系の方へ平衡移動するため、表面に緻密層ができやすいという欠点と、同じ原液から透水性・分画分子量を広範囲に持つ種々の半透膜を製造し得ないという欠点を有するものであった。

【0006】

【発明が解決しようとする課題】本発明者らは、上記欠点を解析し、鋭意検討した結果本発明に到達した。特に、透水性、分画分子量を広範囲にとることができ、かつ、目づまりや汚れがおこりにくい、ポリスルホン系樹脂半透膜の製造方法を提供することを目的とする。

【0007】

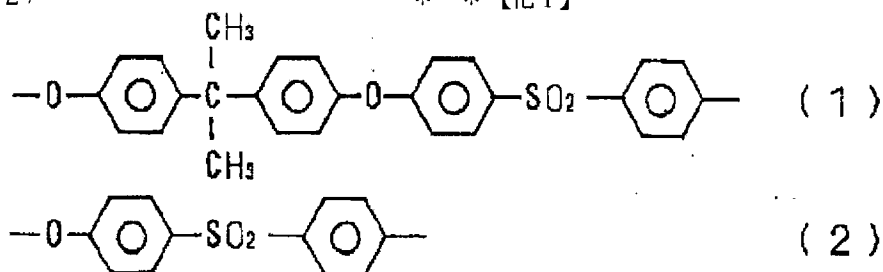
【課題を解決するための手段】本発明は次の構成を有する。すなわち、「ポリスルホン系樹脂と親水性高分子を混和溶解した溶液を製膜原液として用い、成形した膜を熱架橋することを特徴とするポリスルホン系樹脂半透膜の製造方法。」

【0008】

【発明の実施の形態】本発明においてポリスルホン系樹脂半透膜を製造するために用いる製膜原液は、基本的にはポリスルホン系樹脂、親水性高分子および溶媒からなる3成分系で構成される。さらに、成膜原液中に、添加剤を加えることも好ましい。

(1)、または(2)

\* \* 【化1】



の繰り返し単位からなるものであるが、官能基を含んでいたり、アルキル系のものであってもよく、特に限定するものではない。

【0010】親水性高分子は、ポリスルホン系樹脂と相溶性があり、かつ親水性を持つ高分子である。ポリビニルピロリドンが一番良く、他に変性ポリビニルピロリドン、共重合ポリビニルピロリドン、ポリ酢酸ビニル、ポリエチレングリコール等が挙げられるが、これらに限定されるものではない。

【0011】溶媒は、ポリスルホン系樹脂及び親水性高分子を共に溶解する溶媒である。ジメチルスルホキシド、ジメチルアセトアミド、ジメチルホルムアミド、N-メチル-2-ピロリドン、ジオキサン等、多種の溶媒が用いられるが、特にジメチルアセトアミド、ジメチルスルホキシド、ジメチルホルムアミド、N-メチル-2-ピロリドンが望ましい。

【0012】添加剤は、溶媒と相溶性を持ち、親水性高分子の良溶媒となり、かつ、ポリスルホン系樹脂の非溶媒又は膨潤剤となるものであれば何でも良く、例えば、水、メタノール、エタノール、イソプロパノール、ヘキサノール、1, 4-ブタンジオール等がある。生産コストを考えると水が最も望ましい。添加剤は、ポリスルホン系樹脂に対する凝固性を考え合わせた上で選択すれば良い。

【0013】これらのおのおの組合せは任意であり、上記の性質をもつ組合せを考えるのは、同業者にとって容易なことである。また、溶媒・添加剤は、2種類以上の化合物の混合系でも良い。

【0014】該製膜原液の組成として、ポリスルホン系樹脂は、製膜可能でかつ膜としての特性を有する濃度範囲であれば良く、5~50重量%である。高い透水性、大きな分画分子量を得るためにはポリマー濃度は下げるべきで、この場合望ましくは5~20重量%である。5重量%未満では、製膜原液の十分な粘度を得ることができず、膜を形成できなくなる。また、50重量%を越えると貫通孔を形成しにくくなる。

【0015】親水性高分子は、特にポリビニルピロリドンの場合、GAF社から分子量36万、16万、4万、1万のものが市販されており、これを使うのが便利であるが、もちろんそれ以外の分子量のものを使用してもか

して増粘効果もあるため、添加量は高分子量のものを用いるほど少量で良く、かつまた相分離現象の温度依存性の逆転も顕著になるため透水性の高い膜を得るためには有利である。ポリビニルピロリドンの添加量は、1~20重量%、特に3~10重量%が望ましいが、用いるポリビニルピロリドンの分子量に左右される。一般に添加量が少なすぎる場合、分子量が低すぎる場合は相分離の逆転現象は得難く、ポリマー濃度が高く、ポリマー分子量が大きすぎると、製膜後の洗浄が困難となる。それ故、分子量の異なるものを混合して役割分担し用いるのも一つの方法となる。

【0016】以上2つの高分子を溶媒に混合溶解する。ここへ、添加剤を添加することが好ましいが、特に水の場合、ポリスルホン系樹脂にとって凝固性が高いため、7重量%以下、特に1~5重量%が望ましい。凝固性が小さな添加剤を用いるときは添加量が多くなることは容易に推測される。

【0017】本発明では、この第4成分が、添加されるため、親水性高分子の量を少なくすることができる。添加剤の濃度が高くなるにつれ、製膜原液の相分離温度は低下してくる。相分離温度の設定は、求める膜の透水性や分画分子量により随意にすればよく、例えば、高い透水性・分画分子量を得るためには製膜時に相分離を強力に促進するため低い相分離温度を設定すれば良い。また、凝固浴の温度を高くしても同様の効果は得られる。本発明で用いる製膜原液は、低温で均一系となるため、原液安定性も良い。

【0018】以上の条件のもとでポリスルホン系樹脂半透膜を得る。製膜操作は、公知技術を用いれば良い。平膜については、該製膜原液を平坦な基板上に流展し、その後凝固浴中に浸漬する。中空糸膜については、中空形態を保つため、注入液を用いる。注入液は、製膜原液に対して凝固性の高いものより、低いものを用いた方が紡糸安定性は良いが、凝固浴温度・相分離温度・口金温度との相関で中空糸膜内壁の平滑性が変化するので、適宜最良組成を決めれば良い。ポリスルホン系樹脂に不活性なデカン・オクタン・ウンデカン等の炭化水素を用いても良い。また気体を注入して中空形態を保持させてもよい。乾式長は0.1~20cmであり、特に0.5~5cmが紡糸安定性も良く、さらに望ましい。同一組成、同一

SS  
CC  
aa  
nn  
nn  
ee  
dd  
11  
22  
33  
44  
55  
66

孔する孔の直径は大きくなる傾向がある。

【0019】かかる方法で得たポリスルホン系樹脂半透膜は、膜中に親水性高分子を残存させることによって、水濡れ性が改善され、熱により架橋されることにより、水に対して不溶化処理が施されてなるものである。

【0020】

【実施例】以下の実施例によって本発明をさらに詳細な説明する。

【0021】以下、用いた測定法は次のとおりである。

【0022】(1) 透水性

中空糸膜の場合は、両端に環流液用の孔を備えたガラス製のケースに該中空糸膜を挿入し、市販のポッティング剤を用いて小型モジュールを作製し、37℃に保って中空糸内側に水压をかけ膜を通して外側へ透過する一定時間の水の量と有効膜面積および膜間圧力差から算出する方法で透水性能を測定した。

【0023】平膜の場合は、攪拌円筒セルを用いて同様にして測定した。

【0024】実施例1

ポリスルホン（ユーデルP-3500）15部、ポリビニルピロリドン（K90）8部、1,4-ブタンジオール7部をジメチルアセトアミド70部に加え、加熱溶解した。この製膜原液は、70℃で相分離するように1,4-ブタンジオールをさらに微量添加して調製した。調製された原液を外径1.0mm、内径0.7mmの環状オリフィスからなる口金孔内から注入液としてジメチルアセトアミド/水=85/15を注入しつつ吐出させ、口金面から1.0cm下方に設置した51℃に保温した水を有する凝固浴に通過させ、通常の方法で水洗後カセにまき取り、中空糸条膜を得た。口金は60℃に保温した。得られた中空糸膜の、透水性は1320ml/m<sup>2</sup>・hr・mm

Hgの性能を示した。

【0025】更に、この中空糸膜を175℃5時間処理しポリビニルピロリドンを熱架橋したところ、透水性は15800ml/m<sup>2</sup>・hr・mmHgになった。水洗後溶出物試験を行ったところ、溶出物はほとんどなかった。

【0026】比較例1

ポリスルホン12部、ポリビニルピロリドン6部をN-メチルピロリドン82部に加え、加熱溶解した。この原液を50℃に保温し、実施例1と同様にして製膜した。

10 透水性は600ml/m<sup>2</sup>・hr・mmHgと低いものであった。

【0027】比較例2

比較例1の原液で、原液と室温に保って同様に製膜した。透水性は250ml/m<sup>2</sup>・hr・mmHgであった。

【0028】比較例3

ポリスルホン15部、ジメチルアセトアミド83部に水2部を加え、加熱溶解し比較例1と同様にして製膜したが、透水性は25ml/m<sup>2</sup>・hr・mmHgと低いものしか得られなかった。

20 【0029】比較例4

比較例1～2の膜に、ポリビニルピロリドンの抽出、熱架橋処理と施すと、透水性はほとんど0となった。

【0030】

【発明の効果】本発明はポリスルホン系樹脂半透膜の、透水性、分画分子量を広範囲にとることができる。原液条件、製膜条件を適切に選ぶことにより、複合膜の支持体も製造可能である。かつ、得られるポリスルホン系樹脂半透膜は、目づまり、汚れに対して強いため、逆浸透膜から、高性能限外濾過膜（あるいは精密濾過膜）まで、一般産業用途及び医療分野の血液成分分離膜として使用することができる。

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